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1. Your reference — Thermal Imaging

2. Patent application number *(The Patent Office will fill this part in)* — 0402960.9 — 10 FEB 2004

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

   Plastic Logic Limited
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   Cambridge
   CB4 0FX

   Patents ADP number *(if you know it)* 829392001

   If the applicant is a corporate body, give the country/state of its incorporation — UK

4. Title of the invention

   Thermal Imaging of Catalyst in Electroless Deposition of Metal Films.

5. Name of your agent *(if you have one)* — Philip Slingsby

   "Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

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   WC1N 2LS

   Patents ADP number *(if you know it)* 1255003

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Signature(s) S Bowes

Date 3/02/04

12. Name, daytime telephone number and e-mail address, if any, of person to contact in the United Kingdom

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Thermal Imaging of Catalyst in Electroless Deposition of Metal Films

The present invention relates to selective electroless deposition of a metallic film on a substrate using a method of laser-patterning a catalytic film.

Electroless metal plating is a popular method of depositing metal films in many industries, including the printed circuit board industry. Laser-patterning electroless plating has been discussed in the prior art in which a laser beam is used to enhance the plating reactions by localized heating in order to form a metallic film.

In Patent No's. US5084299 and US4981715, selective deposition of a conductor on a substrate is disclosed. A polymer layer is initially deposited on a substrate. The polymer is complexed with a palladium-containing compound, which acts as a catalyst for electroless plating of a metallic layer. The upper layer is irradiated and a subsequent developing step removes the non-irradiated regions through a process of chemical wet etching. The irradiated substrate is then exposed to an electroless plating bath to form a metal layer.

In Patent No. US5192581, electroless metal plating occurs selectively by a method of patterning the layered substrate with a laser beam. A protective layer is deposited on the substrate and a catalyst layer is deposited over the protective layer in a predetermined pattern. Electroless deposition may then occur on the predetermined pattern on the layered substrate. The portions of the catalyst layer that have not been irradiated may be stripped by subsequent etching steps. This method allows for the process to occur without the need for photolithography while preventing unwanted electroless sheeting on the dielectric substrate which has inadvertently become catalytic in certain regions.

However, the prior art has many potential failure points. A main feature of the present invention is that no predetermined pattern is required prior to deposition of the catalyst material. This has the benefit of reducing the number of processing steps required. In addition, an added advantage over processes carried out in the prior art is that during

electroless deposition, the metallic film will only grow over the areas that were not exposed to heat. Therefore, no chemical etching step to remove portions of the catalytic layer is required after exposure to the radiation. Finally, the present invention does not require the conductive contacts to be inkjet printed onto the layered substrate (see Patent No. WO02095805). Inkjet printing of contacts often results in low resolution due to the lower degree of accuracy of the printing technique compared to electroless deposition.

The object of the present invention is to provide an improved method of laser-assisted electroless deposition of a metallic layer on a substrate.

According to a first embodiment of the present invention a process of patterning an electroless metal layer is disclosed which includes providing a substrate on which a thermal imaging layer is deposited followed by the deposition of a catalytic layer. On exposure of the layered substrate to a laser beam the underlying thermal imaging layer converts radiation from the laser beam to heat, in order to create a chemical reaction in the catalytic layer. The said reaction changes the chemical form of the catalyst rendering the exposed regions of the catalyst inactive. A regenerating solution increases the potency of the unexposed regions of the catalyst layer, while the exposed regions remain inactive. In a subsequent developing step, the substrate is developed in a solution of metal ions initiating the growth of a metal film in the unexposed regions of the catalyst, thereby allowing electroless deposition of a metal layer to occur.

A further aspect of the present embodiment provides a substrate on which a thermal imaging layer is deposited over a previously deposited catalytic layer. On exposure of the layered substrate to a laser beam the thermal imaging layer generates enough heat to initiate a chemical reaction in the catalytic layer to convert the exposed areas into an inactive catalytic state. The exposed regions of the catalyst are therefore ineffective to the subsequent regeneration and metallic solution developing steps. As seen previously, the metal layer is only formed on the unexposed regions of the catalytic layer.

A second feature of the present invention incorporates the deposition of a heat sensitive catalytic layer on a substrate, thereby excluding the need for the deposition of two separate layers, namely a catalytic material and a thermal imaging layer. Exposure of the catalytic layer renders the exposed regions ineffective to the subsequent developing steps, as described above. A developing step consisting of submerging the substrate in a regeneration solution is carried out with the result of enhancing the catalytic properties of the unexposed regions of the catalyst. The substrate and selectively laser-patterned heat sensitive catalytic layer is again further developed in a metallic solution. A reaction between the solution of metal ions and the catalytic layer ensures that the catalyst will be unable to act as a template layer from which a metal film will grow.

To help understanding of the invention, a specific embodiment thereof will now be described by way of example and with reference to the accompanying drawings, in which:

Figure 1 illustrates processing steps for electroless metal plating on a substrate that incorporates a thermal imaging layer positioned below the catalyst layer.

Figure 2 shows processing steps for electroless metal plating on a substrate that incorporates a thermal imaging layer positioned above the catalyst layer.

Figure 3 illustrates processing steps for electroless metal plating on a substrate that incorporates a heat sensitive catalyst layer.

With reference to the drawings, the first embodiment of the present invention is illustrated in Figure 1. The first embodiment provides a catalytic layer and an underlying thermal imaging layer deposited on a substrate. The absorbed radiation is converted to heat in the thermal imaging layer and reacts to render the exposed regions of the catalytic layer inactive. This results in the patterning of an electroless metal layer on the substrate.

A substrate 1 is coated with a thermal imaging material 2. The substrate may be either glass or a polymer film. A thermal imaging material is one that is able to convert absorbed radiation to heat. The thermal imaging layer (TIL) is preferably coated from solution by standard thin film coating techniques, including but not limited to spin, dip,

blade, bar, slot-die, or spray coating, inkjet, gravure, offset or screen printing. The thermal imaging material generates heat from absorbed IR radiation, for example in the form of a focused laser beam 4 focused through a lens 5, or alternatively from a pattern of light generated by passing a light beam through a shadow mask. This results in a change in the chemical form in the above lying catalytic layer 3. The material of the thermal imaging layer must be chosen such that there are good adhesive properties between the thermal imaging layer and the substrate. By choosing light of infrared wavelengths such as 830 nm or 1064 nm, the laser light is unable to be absorbed by most conjugated polymers. Therefore, degradation of underlying electroactive layers within the multilayer stack on the substrate may be avoided. Although other wavelengths in the visible and ultraviolet spectral range may also be used, care needs to be taken in such cases to minimize exposure of the multilayers to light, particularly in the presence of oxygen to avoid degradation by processes such as photooxidation. To ensure that radiation of the required wavelength is absorbed, a dye may be added to the polymer film that absorbs at 830 nm. An example of a switchable material according to this invention is a polystyrene film. The absorption of the laser light is enhanced by mixing an infrared laser dye (SDA4554) into the solution from which the polystyrene is deposited. Alternatively, a more polar polymer may be used, such as a poly(vinyl phenol) film doped with a suitable corresponding infrared laser dye (SDA4927).

A layer of catalyst 3 which can initiate electroless deposition is deposited from solution on top of the thermal imaging layer and dried in order to produce a catalytic film. The properties of the catalytic layer must be such that it will react with a solution of metal ions to initiate production of a metal film. The catalytic layer is preferably coated from solution by standard thin film coating techniques, including but not limited to spin, dip, blade, bar, slot-die, or spray coating, inkjet, gravure, offset or screen printing. The properties of the catalyst include heat-sensitive properties, such that on exposure to elevated temperatures, the catalytic film will no longer be active as a catalytic material. When heat is generated in the underlying thermal imaging layer from exposure to a focused laser beam, a chemical reaction is promoted in the catalytic layer to change the chemical form of the catalytic material, rendering the material inactive as a catalyst. The

selective exposure of the multilayered substrate results in the patterning of the upper catalytic layer. The selective laser-patterned upper layer consists of alternating regions of active and inactive catalyst. In subsequent developing steps the substrate and multi-layered films are exposed to a regenerating solution. Exposure to the regenerating solution may occur by techniques such as those involving methods of dipping the substrate into the solution or techniques such as inkjet printing the regenerating solution on top of the substrate. The regenerating solution has the effect of increasing the potency of the unexposed regions of the catalytic layer. A further developing step is conducted by exposing the substrate to a developing solution of metal ions. This again may occur as a result of a number of techniques, including but not limited to methods of dipping the substrate into the solution and inkjet printing the solution on to the substrate. A suitable developing solution consists of various metal ions, such as, but not limited to copper ions or gold ions. During exposure of the substrate to the developing solution, the growth of a metal film is initiated from the catalytic layer in the regions unexposed to the IR radiation, resulting in a predetermined patterned metal layer, forming the source and drain or gate electrodes.

A further aspect of the present embodiment provides a catalytic layer 3 that is deposited directly onto the substrate, followed by the deposition of a thermal imaging layer 2. The unexposed regions of the catalytic layer are able to initiate electroless deposition.

A substrate 1 is coated with a layer of catalyst 3. The substrate may be either glass or a polymer film. The catalytic layer is preferably coated from solution by standard thin film coating techniques, including but not limited to spin, dip, blade, bar, slot-die, or spray coating, inkjet, gravure, offset or screen printing. The properties of the catalytic layer must be such that it will react with a solution of metal ions to initiate production of a metal film. In addition, the catalyst must have heat-sensitive properties, such that on exposure to elevated temperatures, the catalytic film will no longer be active as a catalytic material.

A thermal imaging material is then deposited over the catalytic layer. As stated above, a thermal imaging material is one that is able to convert absorbed radiation from the laser beam to heat. The thermal imaging layer (TIL) is preferably coated from solution by standard thin film coating techniques, including but not limited to spin, dip, blade, bar, slot-die, or spray coating, inkjet, gravure, offset or screen printing. The material of the thermal imaging layer must be chosen such that there are good adhesive properties between the thermal imaging layer and the substrate. In addition, the TIL must contain a moiety that enables the layer to absorb the focused IR radiation. To ensure that radiation of the required wavelength is absorbed, a dye may be added to the polymer film that absorbs at 830 nm. A switchable material such as a polystyrene film may be used for the TIL. The absorption of the laser light is enhanced by mixing an infrared laser dye (SDA4554) into the solution from which the polystyrene is deposited. Alternatively, a more polar polymer may be used, such as a poly(vinyl phenol) film doped with a suitable infrared laser dye (SDA4927). The thermal imaging material generates heat from absorbed IR radiation, for example in the form of a focused laser beam 4 focused through a lens 5, or alternatively from a pattern of light generated by passing a light beam through a shadow mask. A sufficient amount of heat is generated to render the overlying catalyst ineffective to subsequent developing steps. This results in a change in the chemical form of the overlying catalytic layer 3. This therefore has the result of rendering the exposed regions of the catalytic layer unsusceptible to the formation of a metal film. The selective exposure of the multilayered substrate results in the patterning of the lower catalytic layer. The selective laser-patterned lower layer consists of alternating regions of active and inactive catalyst.

In subsequent developing steps, as described above, the substrate and multi-layered films are exposed to a regenerating solution. Exposure to the regenerating solution may occur by techniques such as those methods of submerging the substrate into the solution or alternatively techniques such as inkjet printing the regenerating solution on top of the substrate. The regenerating solution has the effect of increasing the potency of the unexposed regions of the catalytic layer. After removal of the TIL, a further developing step is conducted by exposing the substrate to a developing solution of metal ions. This

again may occur as a result of a number of techniques, including but not limited to methods of submerging the substrate into the solution or inkjet printing the solution on to the substrate. A suitable developing solution consists of various metal ions, such as, but not limited to copper ions or gold ions. During exposure of the substrate to the developing solution, the growth of a metal film is initiated from the catalytic layer, in the regions unexposed to the IR radiation, resulting in a predetermined patterned metal layer, forming the source and drain or gate electrodes.

A second embodiment of the present invention is illustrated in Figure 3. The second embodiment provides a single heat sensitive catalytic layer on a substrate, thereby excluding the need for the deposition of two separate layers of catalytic material and a thermal imaging layer. The absorbed radiation is converted to heat in the heat sensitive catalytic layer and is used as an alternative way of patterning an electroless metal layer.

A substrate 1 is coated with a heat sensitive catalytic material 9. The substrate may be either glass or a polymer film. A heat sensitive catalytic material is one that is able to convert absorbed radiation to heat while catalyzing a reaction to form a metal layer from a solution of metal ions. The heat sensitive catalytic layer is preferably coated from solution by standard thin film coating techniques, including but not limited to spin, dip, blade, bar, slot-die, or spray coating, inkjet, gravure, offset or screen printing. The heat sensitive catalytic material generates heat from absorbed IR radiation, for example in the form of a focused laser beam 4 focused through a lens 5, or alternatively from a pattern of light generated by passing a light beam through a shadow mask. This results in a change in the chemical form of the deposited catalytic 10. The material of the heat sensitive catalytic layer must be chosen such that there are good adhesive properties between this layer and the substrate. In addition, the heat sensitive catalytic material must contain a moiety that enables the layer to absorb the focused IR radiation. To ensure that radiation of the required wavelength is absorbed, a dye may be added to the polymer film that absorbs at 830 nm. An example of a switchable material according to this invention is polystyrene film. The absorption of the laser light is enhanced by mixing an infrared laser dye (SDA4554) into the solution from which the polystyrene is deposited.

Alternatively, a more polar polymer may be used, such as a poly(vinyl phenol) film doped with a suitable infrared laser dye (SDA4927).

When heat is generated in the heat sensitive catalytic layer from exposure to a focused laser beam, a chemical reaction is promoted in the catalytic layer to change the form of the material, rendering selective regions of the material inactive as a catalyst. The selective exposure of the substrate results in the patterning of the catalytic layer. The patterned layer consists of alternating regions of active and inactive catalyst. In subsequent developing steps the substrate is exposed to a regenerating solution. Exposure to the regenerating solution may occur by techniques such as those involving dipping the substrate into the solution or inkjet printing the solution on top of the substrate. The regenerating solution has the effect of increasing the potency of the unexposed regions of the catalytic layer. A further developing step is conducted by exposing the substrate to a developing solution of metal ions. This again may occur through a number of techniques, including but not limited to dipping the substrate into the solution and inkjet printing the solution on to the substrate. A suitable developing solution consists of various metal ions, such as, but not limited to copper ions or gold ions. During exposure of the substrate to the developing solution, a metal film 7 grows from the catalyst layer in the regions unexposed to the IR radiation, resulting in a predetermined patterned metal layer forming, the source and drain or gate electrodes.

A semiconductor layer, in the case of a top-gate configuration or a dielectric layer, in the case of a bottom-gate configuration may then be deposited directly on top of the electroless deposited metal contacts. These additional layers may be preferably coated from solution by standard thin film coating techniques, including but not limited to spin, dip, blade, bar, slot-die, or spray coating, inkjet, gravure, offset or screen printing. In the case of a top-gate configuration, a gate electrode may then be deposited on top of the semiconductor layer. This requires careful adjustment of the solvents of the underlying layers in order to avoid dissolution or swelling of the semiconducting layer (see US Patent No. 10/176007)..

The above described techniques of patterning the catalytic layer may be used for the formation of the source and drain or gate electrodes in an electronic device. In addition, the techniques described above may be used to produce pixel electrodes and pixel capacitors in electronic circuits.

Possible materials that may be used for the semiconducting layer, includes any solution processible conjugated polymeric or oligomeric material that exhibits adequate field-effect mobilities exceeding 10^{-3} cm^2/Vs and preferably exceeding 10^{-2} cm^2/Vs. Materials that may be suitable have been previously reviewed, for example in H.E. Katz, J. Mater. Chem. 7, 369 (1997), or Z. Bao, Advanced Materials 12, 227 (2000). Other possibilities include small conjugated molecules with solubilising side chains (J.G. Laquindanum, et al., J. Am. Chem. Soc. 120, 664 (1998)), semiconducting organic-inorganic hybrid materials self-assembled from solution (C.R. Kagan, et al., Science 286, 946 (1999)), or solution-deposited inorganic semiconductors such as CdSe nanoparticles (B. A. Ridley, et al., Science 286, 746 (1999)).

Devices such as TFTs fabricated as described above may be part of more complex circuits or devices, in which one or more such devices can be integrated with each other and/or with other devices. Examples of applications include logic circuits and active matrix circuitry for a display or a memory device, or a user-defined gate array circuit. Patterning processes, as described above, may also be used to pattern other circuitry components, such as, but not limited to, interconnects, resistors and capacitors.

The present invention is not limited to the foregoing examples. Aspects of the present invention include all novel and inventive aspects of the concepts described herein and all novel and inventive combinations of the features described herein.

The applicant hereby discloses in isolation each individual feature described herein and any combination of two or more such features, to the extent that such features or combinations are capable of being carried out based on the present specification as a whole in light of the common general knowledge of a person skilled in the art,

irrespective of whether such features or combinations of features solve any problems disclosed herein, and without limitation to the scope of the claims. The applicant indicates that aspects of the present invention may consist of any such individual feature or combination of features. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

Abstract

Thermal Imaging of Catalyst in electroless deposition of metal films

A method for electroless plated metal on a laser-patterned substrate. A substrate is provided on which both a thermal imaging layer and catalytic layer are deposited. On exposure to a laser beam, sufficient levels of radiation are converted to heat in the thermal imaging layer to render the exposed regions of the adjacent catalytic layer inactive. The laser-patterned substrate is then exposed to a solution of metal ions and growth of a metal film is initiated on the unexposed regions of the catalytic layer.

Figure 1

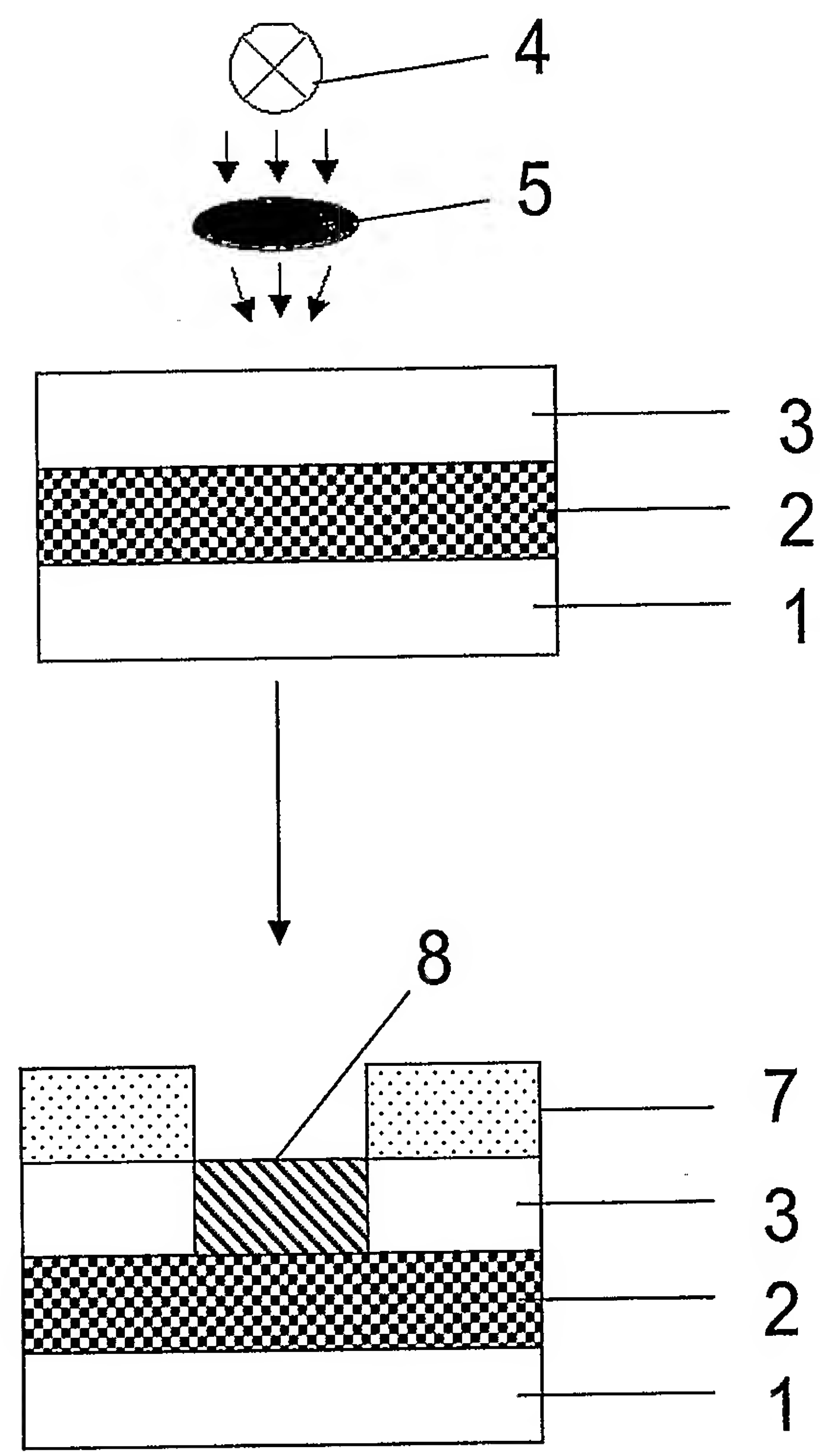

Figure 2

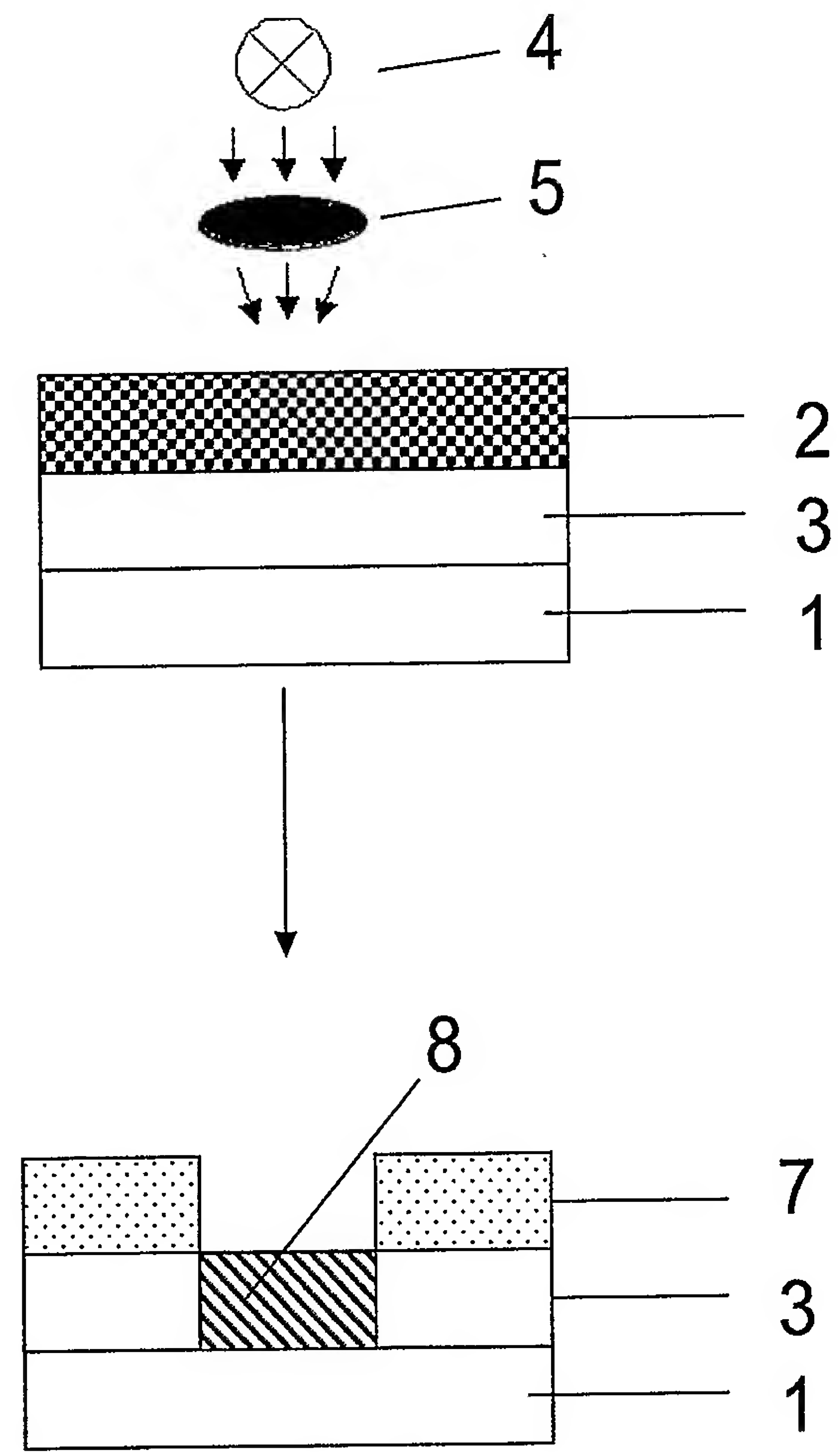

Figure 3